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THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS

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P.M. Lahti

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Presented at Fall, 1989 ONR Contractor's Meeting : Summary of slide presentation.

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18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Organic radicals; organic polyradicals; theoretical and
computational chemistry; unimolecular radical synthesis. JES

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Progress in theoretical and synthetic investigations of organic magnetic species is outlined by slides presented at the Office of Naval Research contractors' meeting of Fall, 1989. Overall, progress was made in synthesis of appropriate groups to allow photochemical and thermal generation of phenoxy radicals in the solid phase. Thermal stability of a variety of substituted phenoxy systems generated by these methods in PPMA matrices was investigated.

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Technical Report #10

THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC
MAGNETIC POLYMERS AND OLIGOMERS

by Paul M. Lahti

Presented at

Office of Naval Research Contractors' Meeting
Autumn, 1989

University of Massachusetts
Department of Chemistry
Amherst, MA 01003

Submitted 6 March 1990

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THEORETICAL INVESTIGATIONS AND ATTEMPTED SYNTHESIS OF ORGANIC MAGNETIC POLYMERS AND OLIGOMERS

by Paul M. Lahti
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

OBJECTIVE:

To investigate the possibilities of generating magnetic information storage materials from basically non-metallic organic precursors, in order to combine the technological usefulness of magnetism with the practical usefulness of organic polymeric materials.

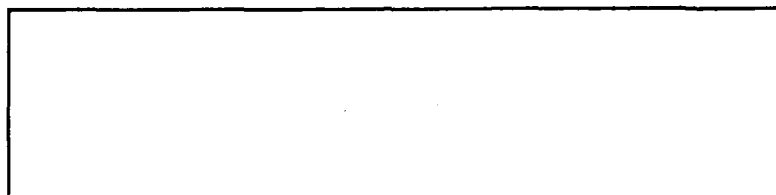
APPROACH:

Theoretical computations allow selection of polyradical polymer structures likely to yield high-spin magnetic properties. Experimentally we synthesize as model compounds small segments of a potential highly magnetic polymer, then test the predictions of theory by standard methods for investigating magnetic properties (electron spin resonance, magnetic susceptibility). Successful predictions for small models will imply that it is worth attempting synthesis of larger polymers predicted to have desirable magnetic properties.

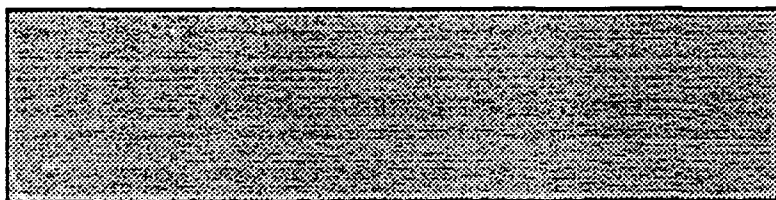
RESULT:

Theory does predict that linkage of several radical units into an oligomer will in many cases yield high-spin organic polyradicals. Experimental generation of such species will constitute the first step toward creating truly polymeric magnetically imaged organic materials.

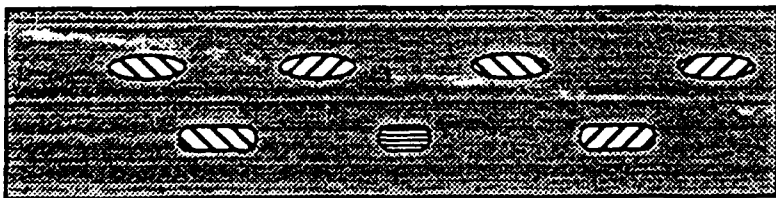
IDEALIZED USE OF POLYRADICAL MAGNETIC MATERIAL PERMANENT READ-ONLY MEMORY



Inert Polymer Backbone
(Support Phase).



Latent Magnetic Precursor
Overlaid on Inert Polymer Base.



Information Encoded
By "Developing" Some
Portion of Precursor
To Become Magnetic.

INTEREST IN ORGANIC FERROMAGNETIC MATERIALS

J. S. Miller, A. J. Epstein, W. M. Reiff

Chem. Rev. 88, 201(1988),
Accts. Chem. Res., 21, 114(1988).

R. Breslow, et al.

Pure Appl. Chem., 54, 927(1982),
J. Am. Chem. Soc., 109, 6412(1987),
J. Am. Chem. Soc., 110, 3970(1988)

Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, V. N. Spector

Nature, 126, 370(1987)

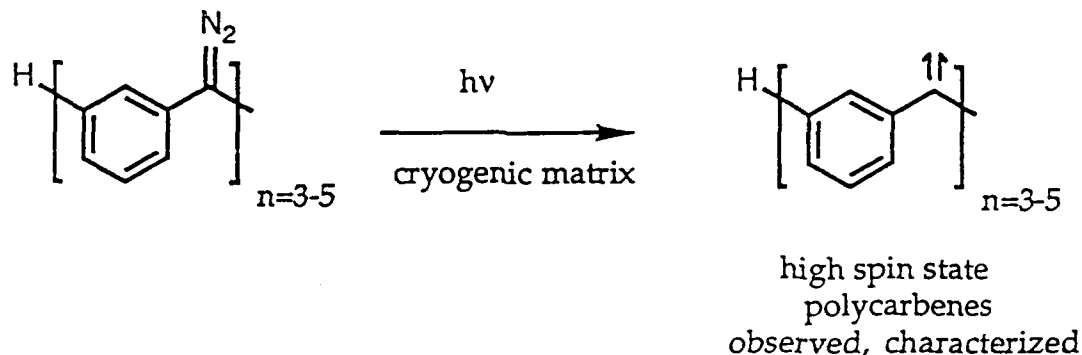
J. B. Torrance, S. Oostra, A. Nazzari

Synth. Metals, 19, 709(1987).

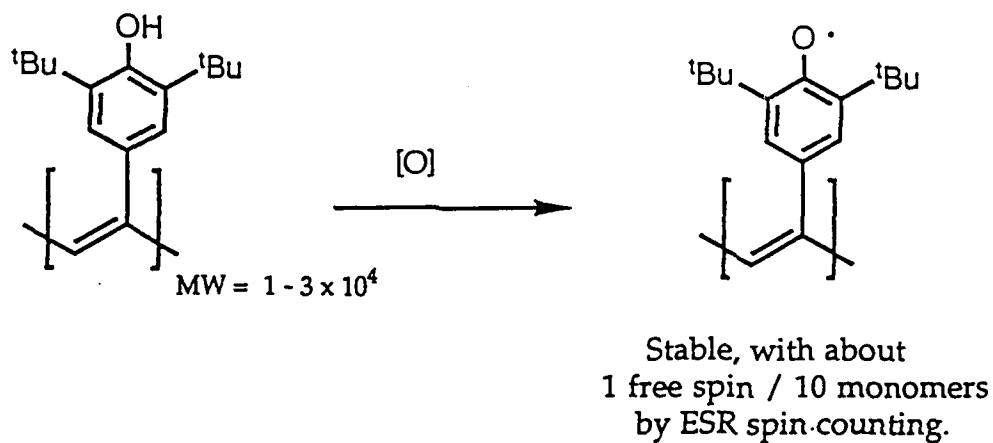
Experimental Work Toward Synthesis of High Spin Polyradicals

Examples include:

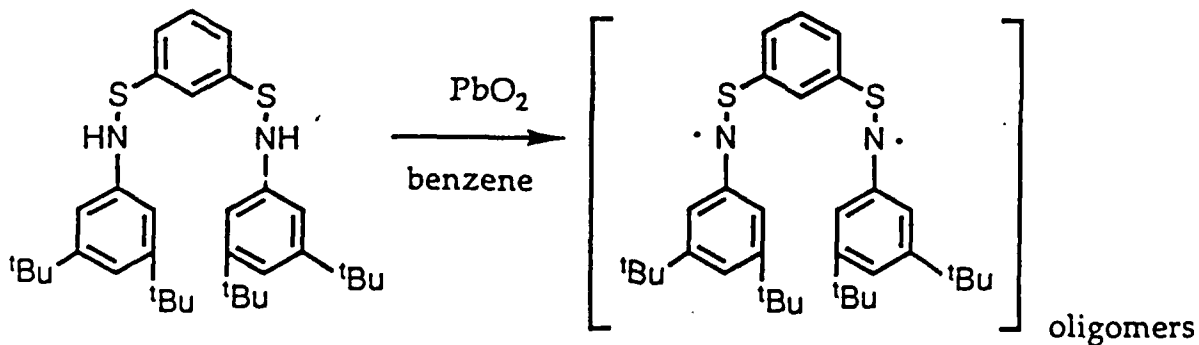
Cf. T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, K. Itoh, *J. Am. Chem. Soc.* 1984, 106, 6449; 1986, 108, 368 and references therein.



H. Nishide, N. Yoshioka, K. Inagaki, E. Tsuchida, *Macromolecules*, 1988, 21, 3120.

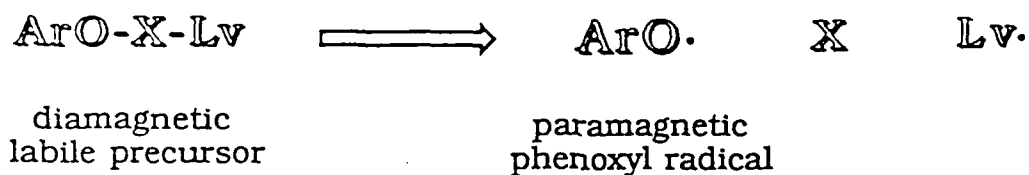


Y. Miura, T. Ohana, *J. Org. Chem.*, 1988, 53, 5770.

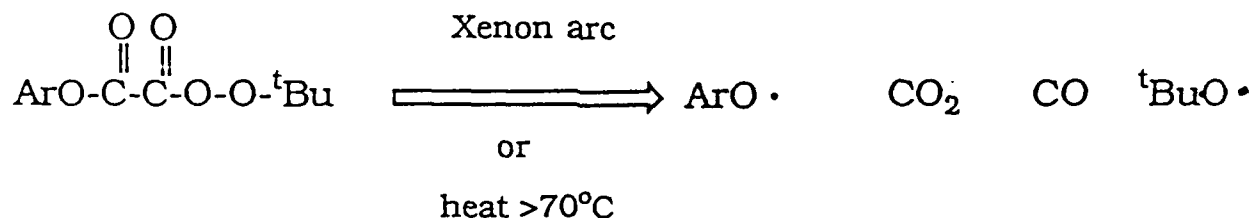


DESIRED: A unimolecular strategy to generate phenoxyl radicals
in solution OR in solid state.

STRATEGY



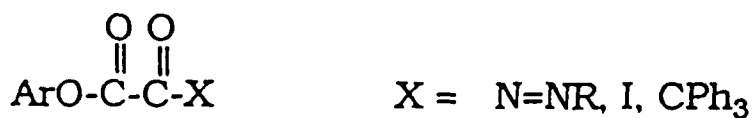
OUR PRESENT METHOD



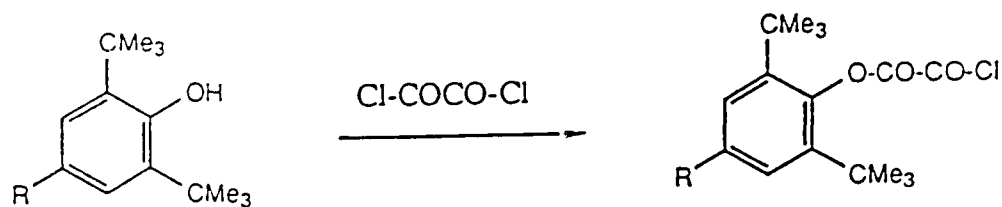
ADVANTAGES

1. Easy and cheap to make
2. Fairly easy to store for some time, soluble in common solvents
3. Some photolability, easy thermal decomposition at $> 70^\circ\text{C}$.

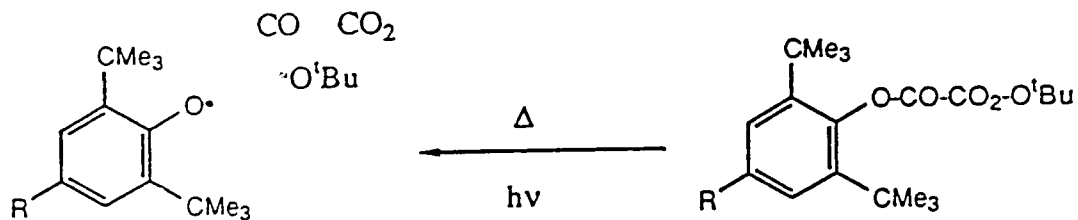
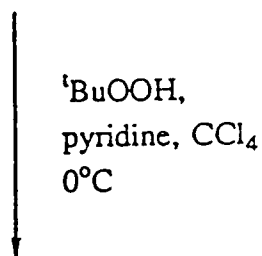
POSSIBLE FUTURE APPROACHES



Synthesis of Peroxyoxalate Precursors for Phenoxy Systems



$\text{R} = \text{CH}_3, \text{C}(\text{CH}_3)_3, \text{H}, \text{C}_6\text{H}_5$

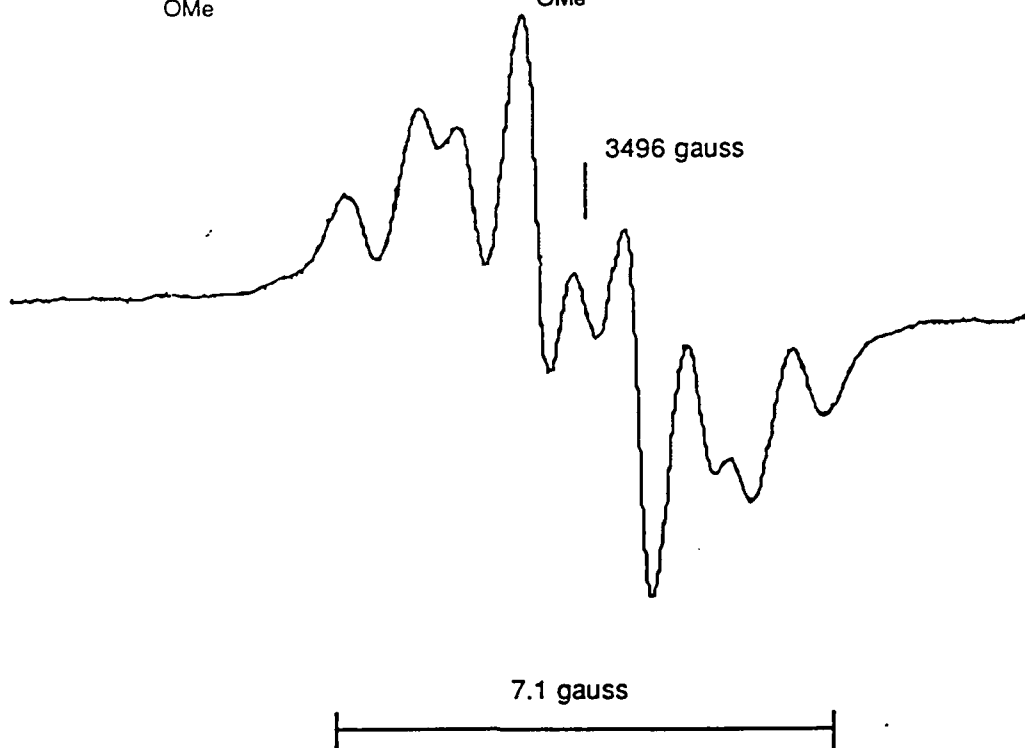
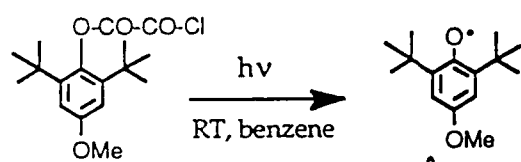


stable for several days
at 25°C in benzene

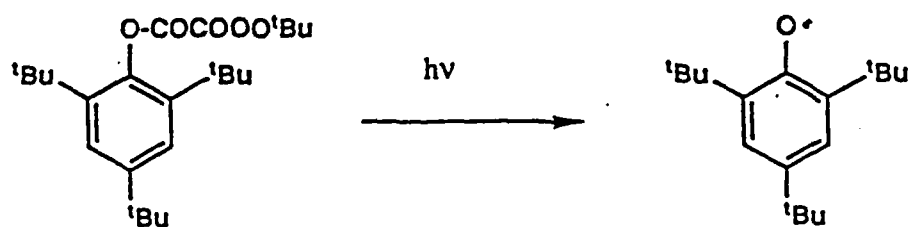
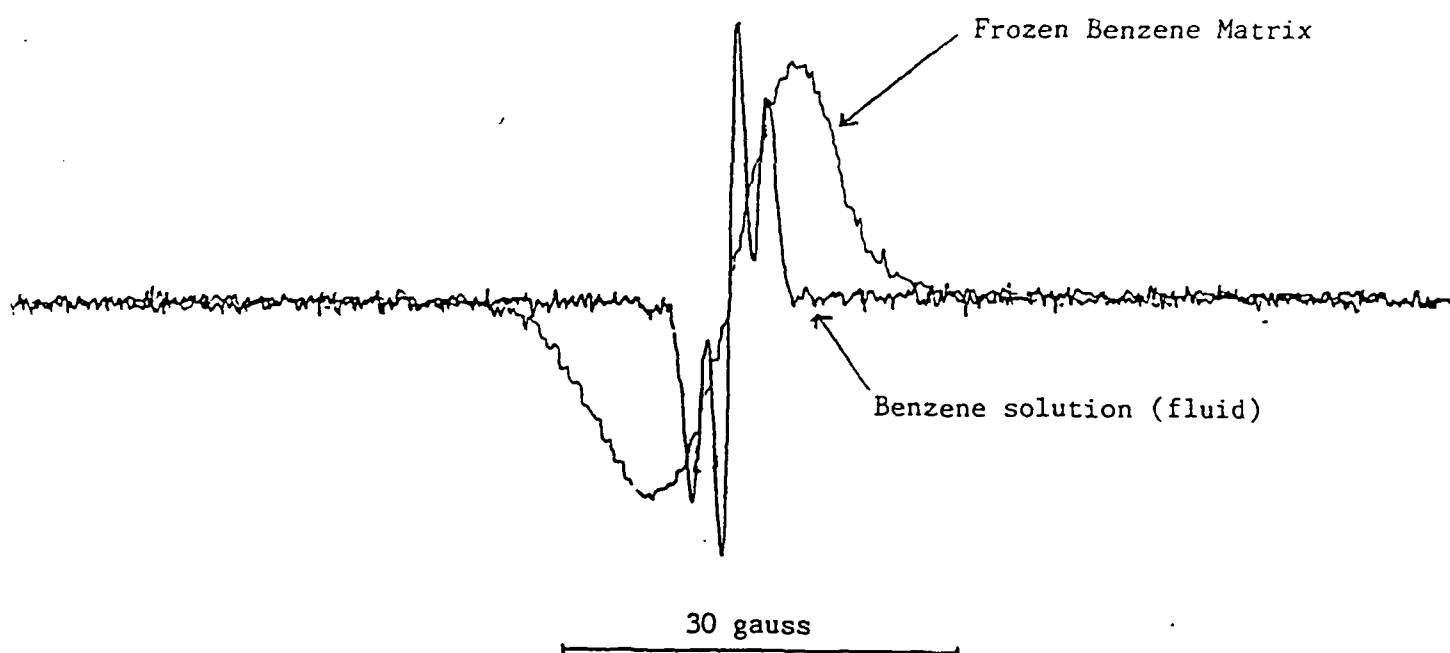
ESR

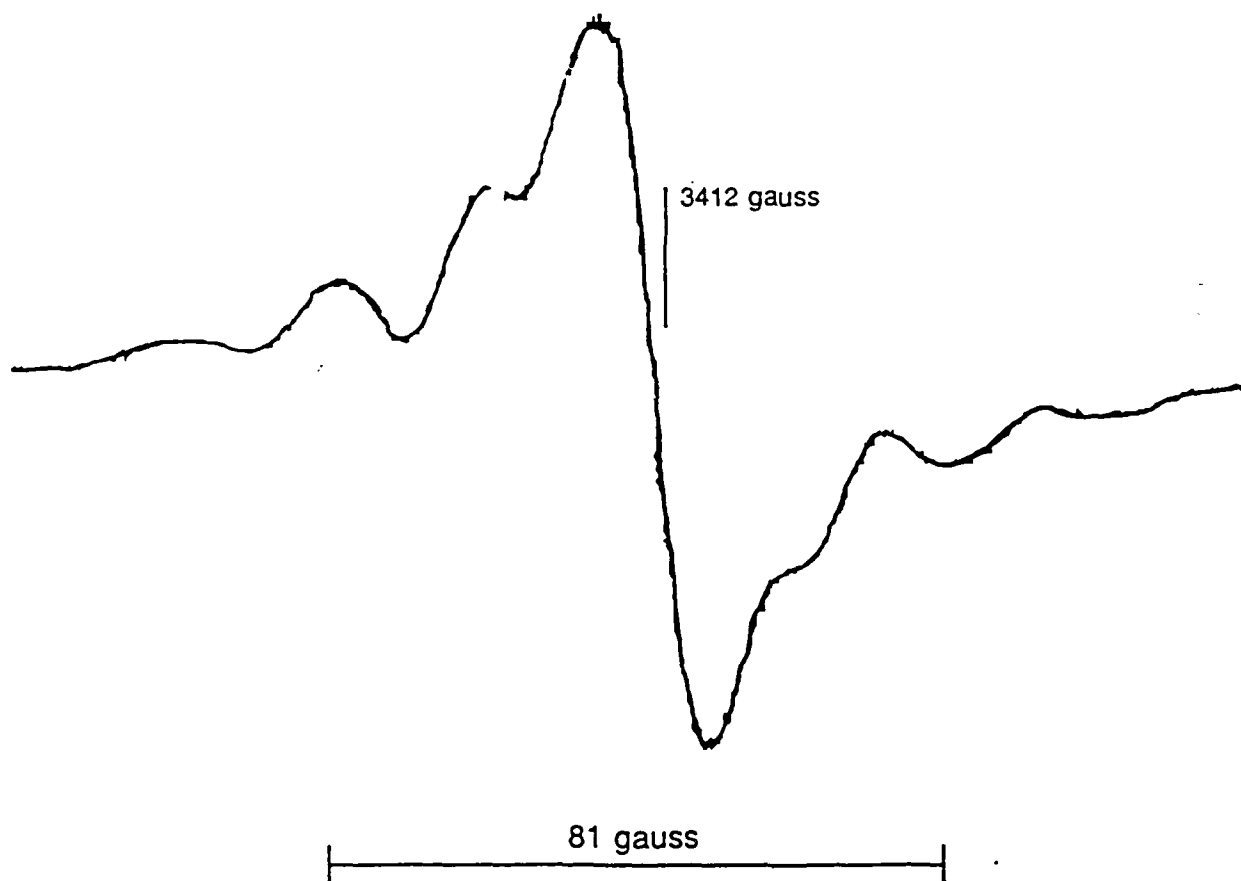
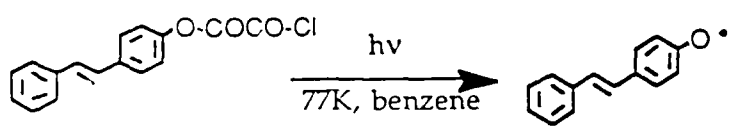
pentane recryst. at -78°C
good room temperature stability

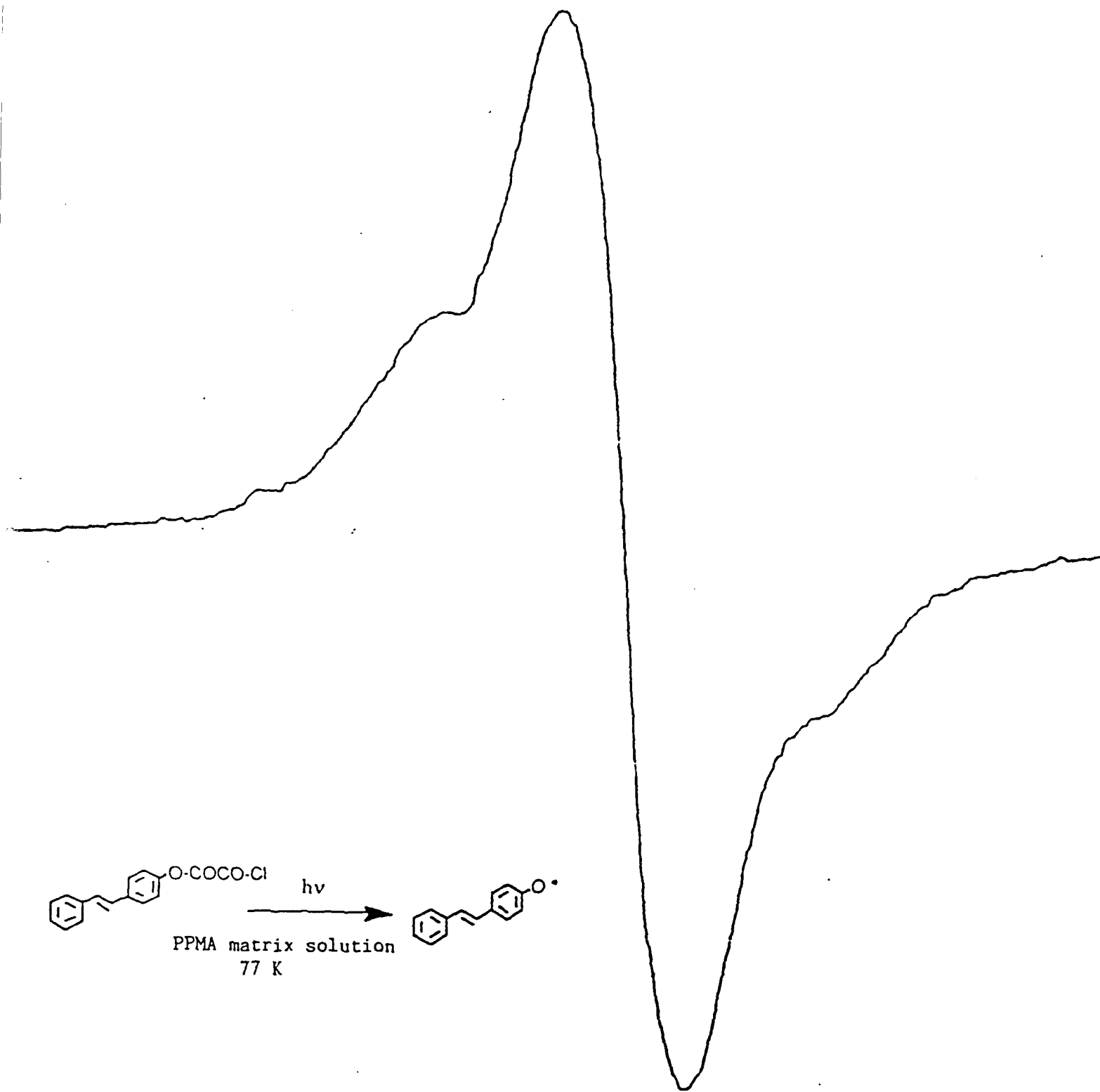
^1H NMR, IR



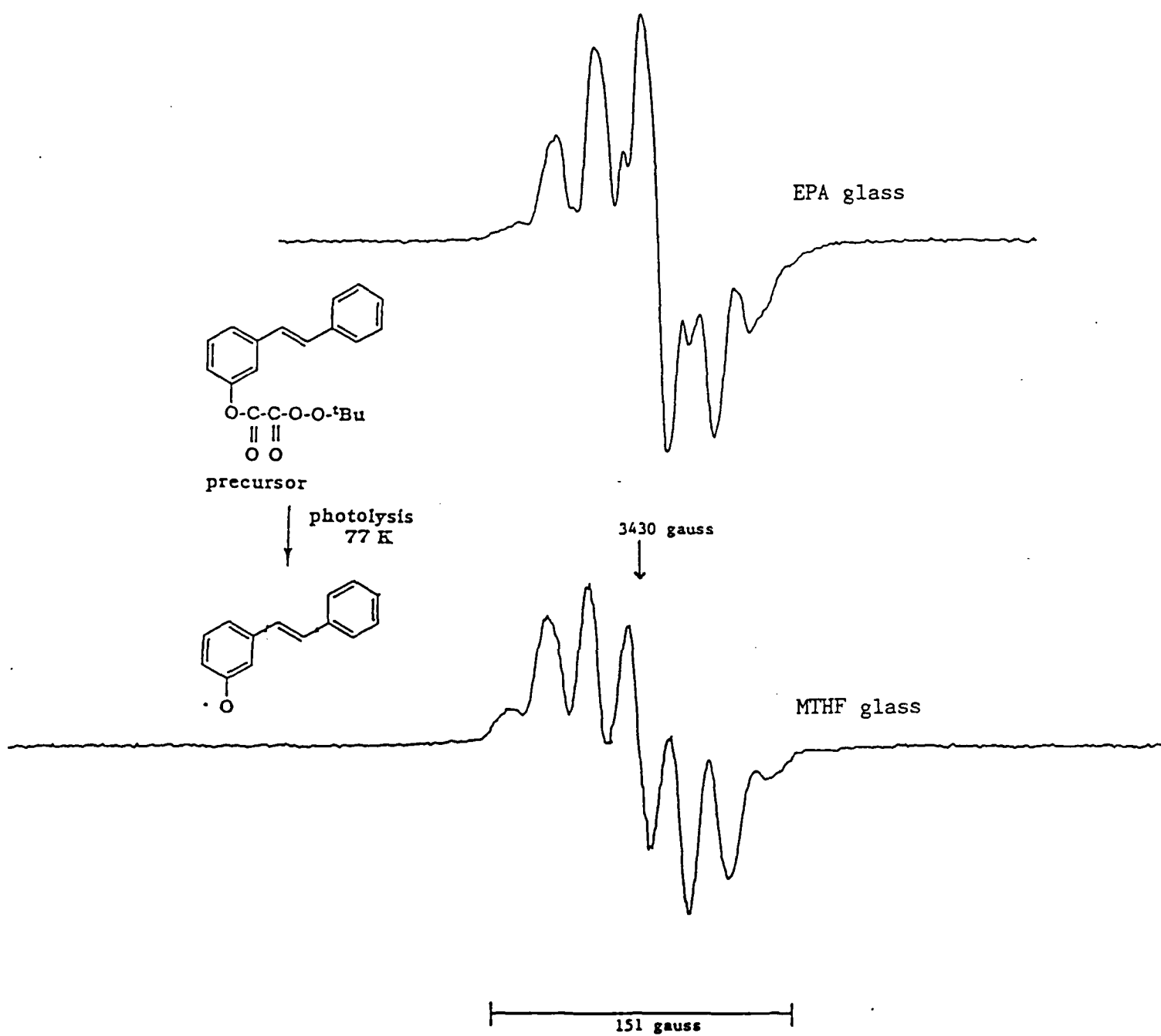
ESR Spectra in rigid matrix are much broader than in solution



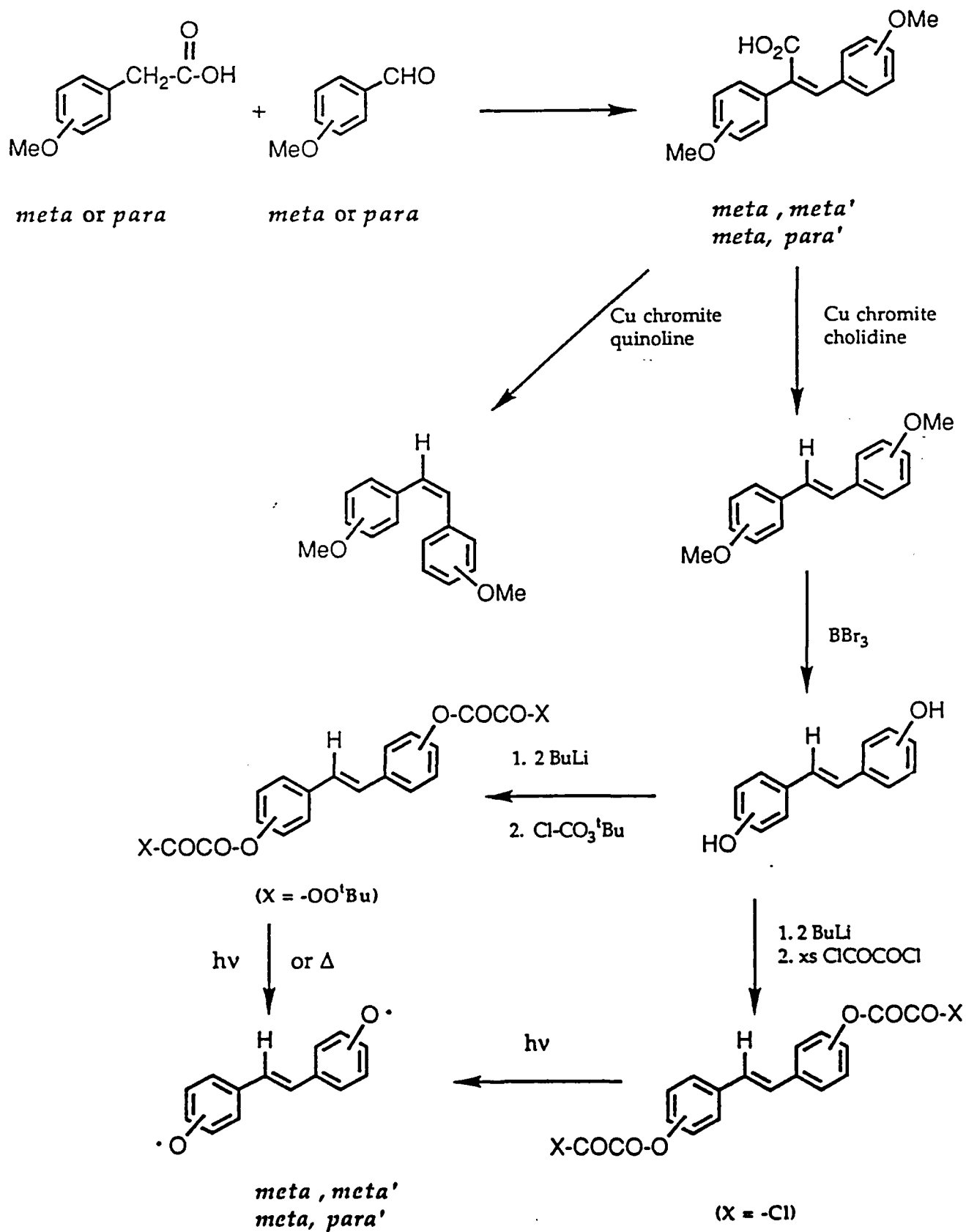


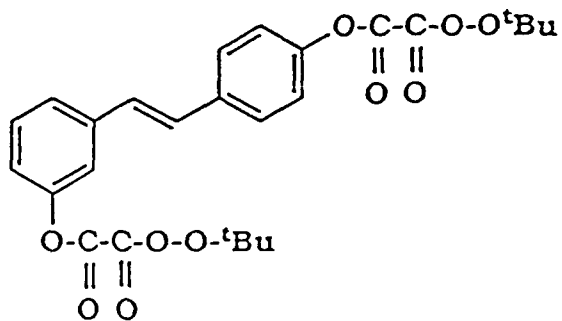


(SIMILAR LOSS OF FINE STRUCTURE IS OBSERVED IN NEAT SAMPLE IRRADIATION)



Synthesis of Dioxy-Stilbenes

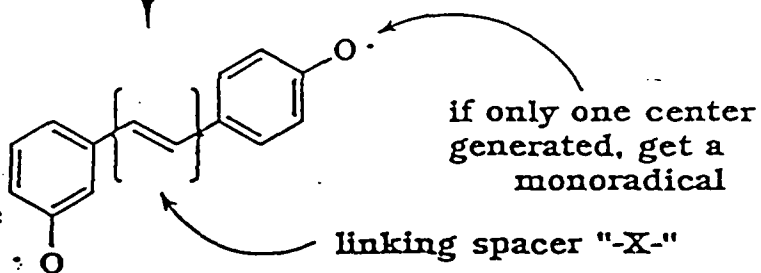




precursor

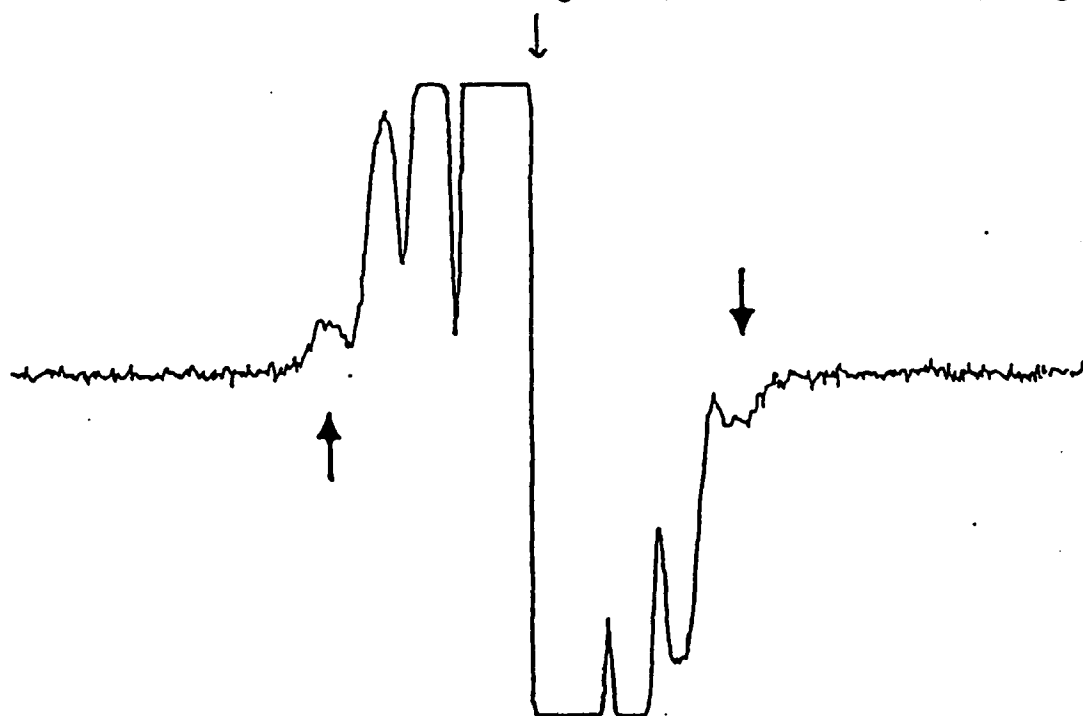
photolysis
77 K

Theory predicts
a paramagnetic
triplet ground state
for this molecule.

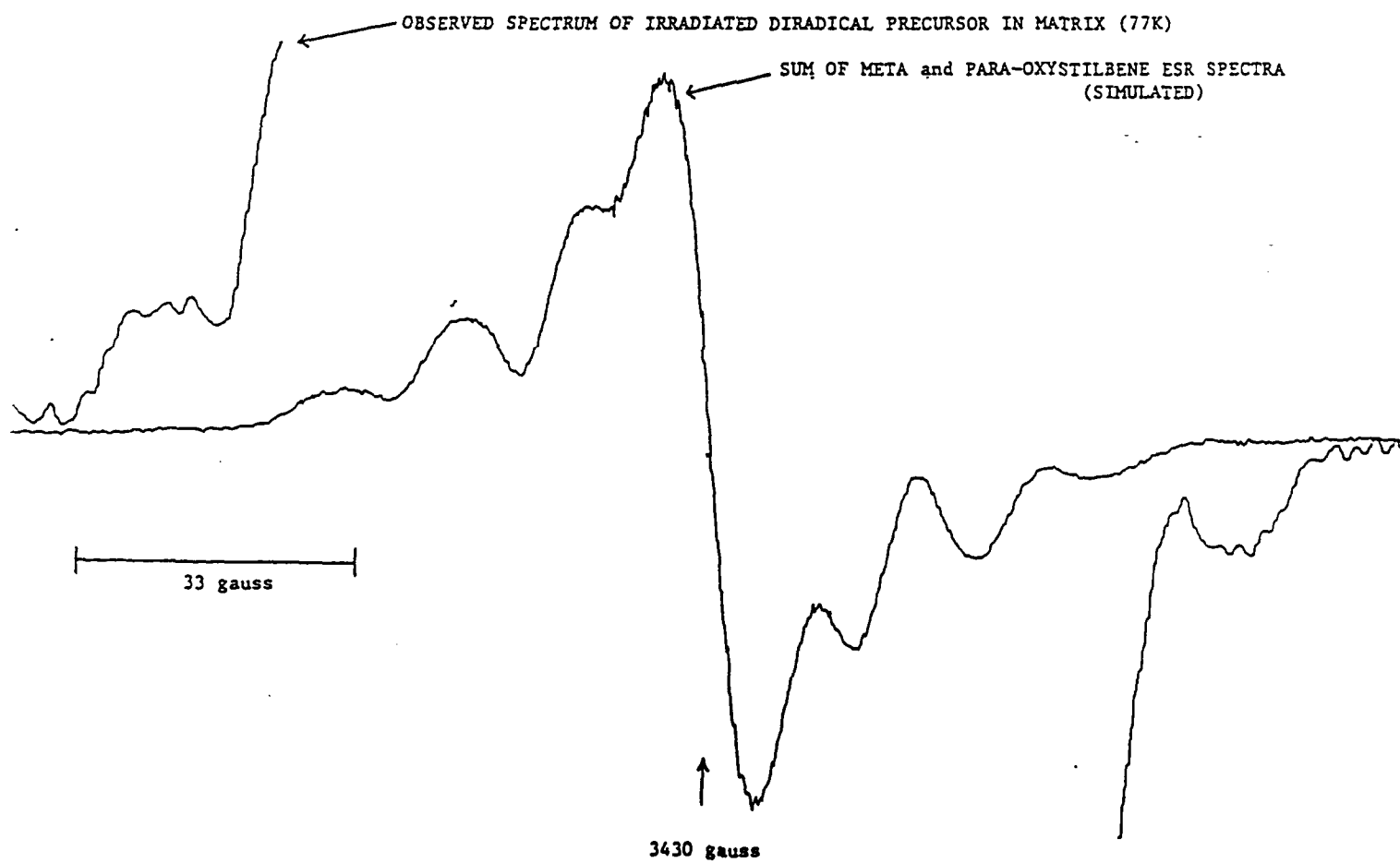


diradical is produced
when both centers
are generated

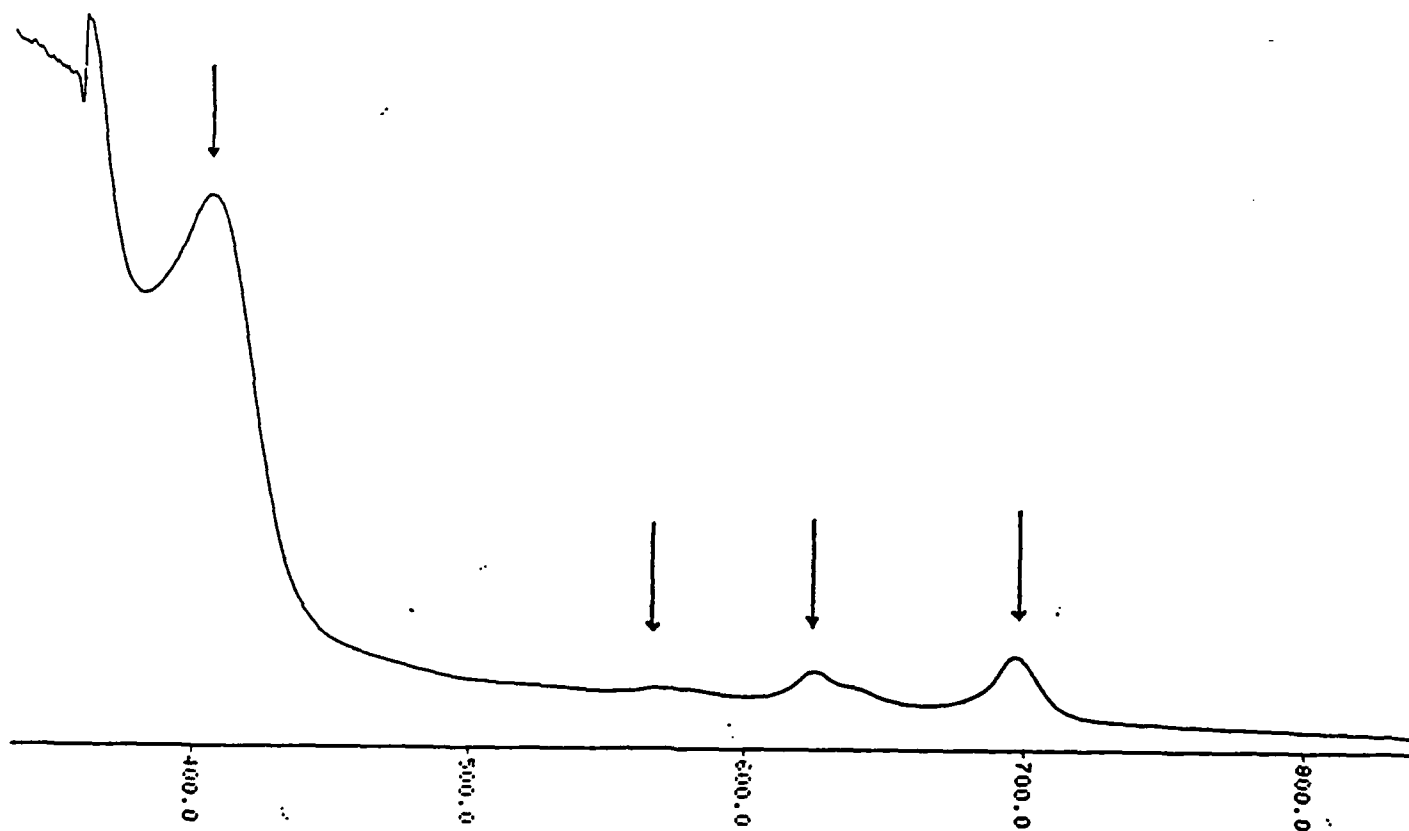
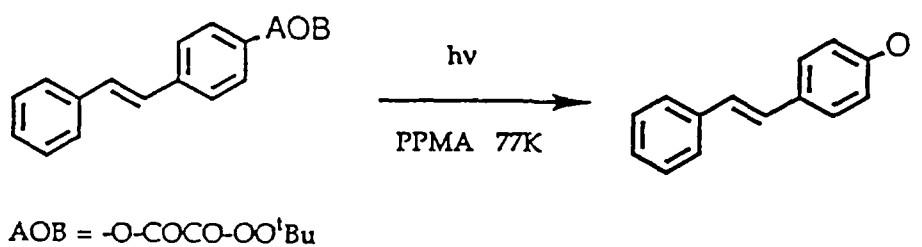
3430 gauss (half-field observed, 25 gauss wide)



204 gauss



STABILITY OF UNHINDERED PHENOXYs IS EASILY MONITORED
IN POLYMERIC MATRIX BY UV-vis SPECTROSCOPY.



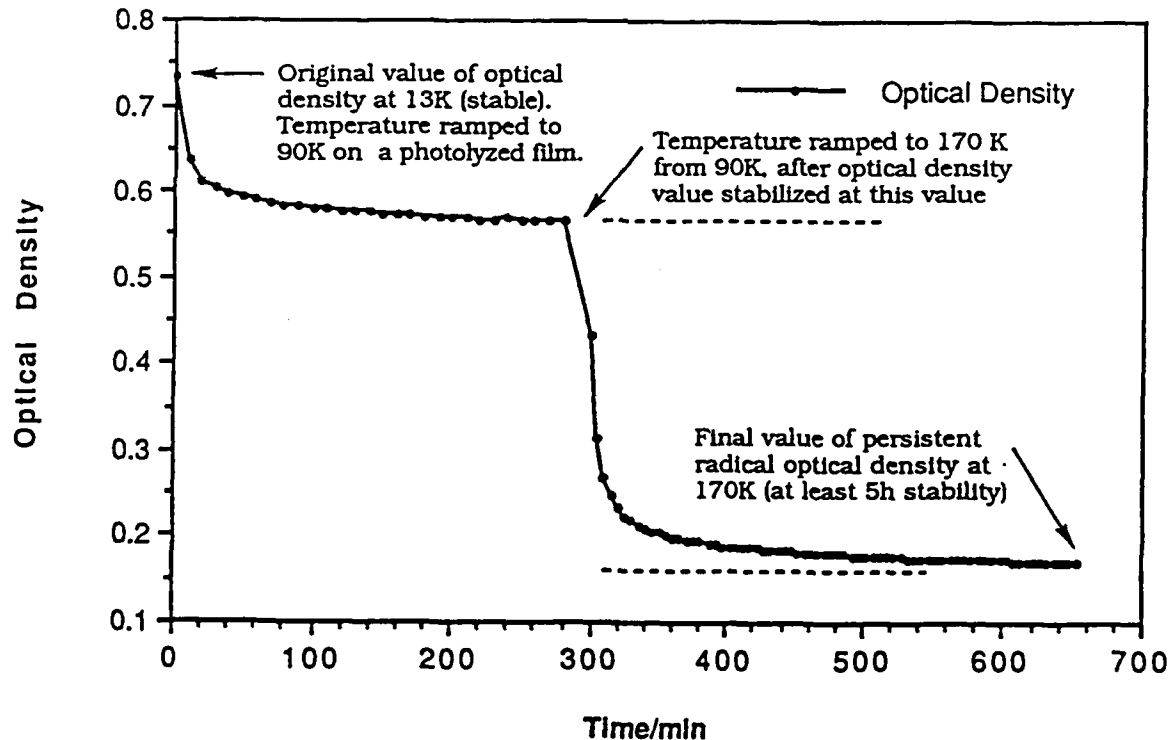
(Arrows indicate the *para*-stilbenoxy absorbances)

UNHINDERED RADICAL STABILITY IN MATRIX

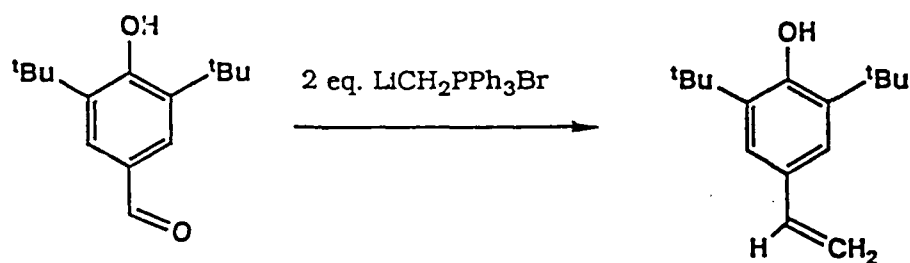
Unhindered *para*-stilbenoxy appears indefinitely stable by UV-vis when generated in PPMA at 13K. When warmed swiftly (<4 min) to 90K, rapid absorbance decay occurs, which slows and leaves the absorbance (radical concentration) approaching an asymptotic value. Warming again to 170K results in the same behavior, with the final result being a much decreased (relative to the 13K value) but still finite amount of radical with stability for at least 5h at 170K. At room temperature, the radical appears to be completely quenched. Similar behavior occurs in polystyrene, but onset of decay behavior is faster. Some decay in both matrices has already occurred by 77K with our typical 10% wt/wt radical-in-polymer mixes.

With some optimization, further increase in stabilization of unhindered radicals in polymer matrix may be possible.

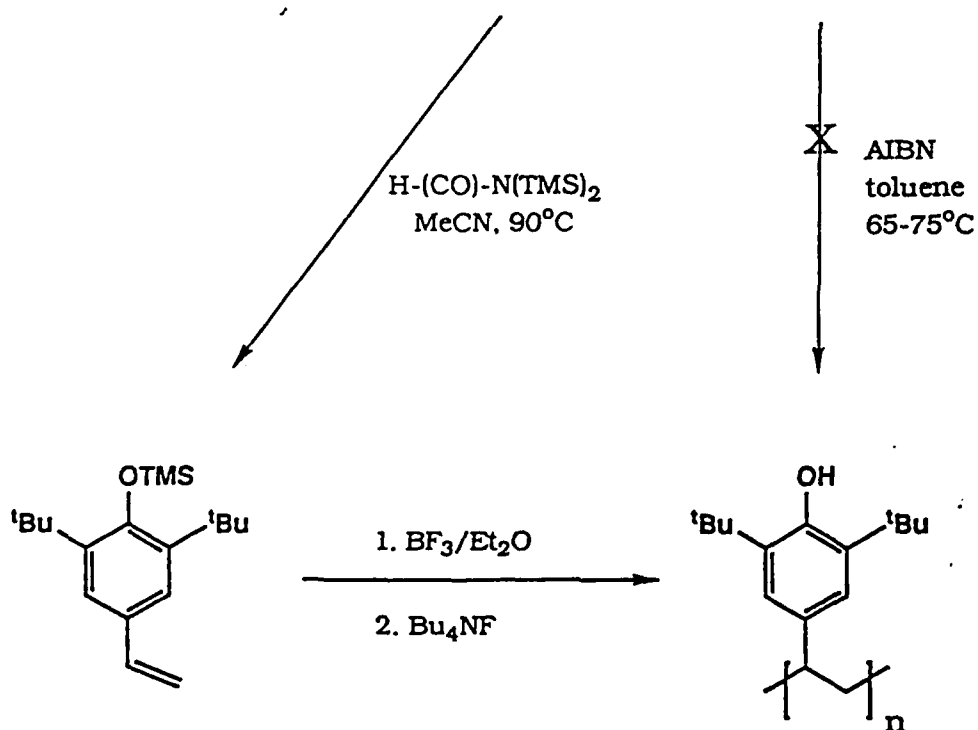
DECAY OF p-STILBENOXY IN PPMA



**A NEW, EFFICIENT SYNTHESIS OF *para*-OLEFINIC
2,6-di-*tert*-Butylphenolic polymer precursors.**



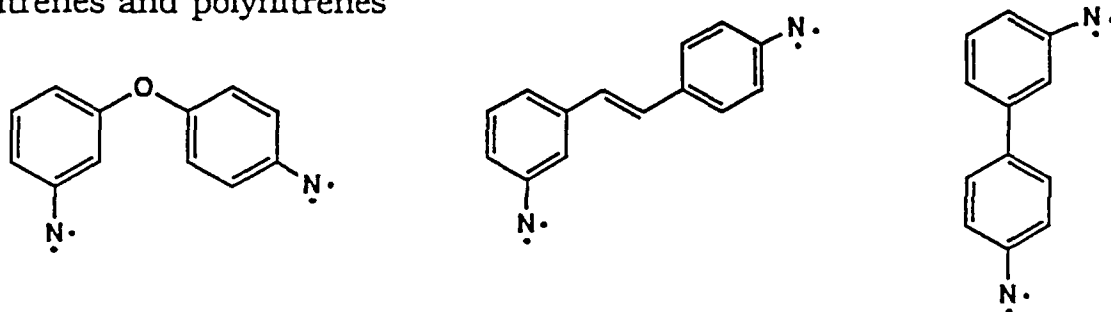
(previously reported in D. Braun,
B. Meier, *Makromol Chem.*, 167, 119(1973))



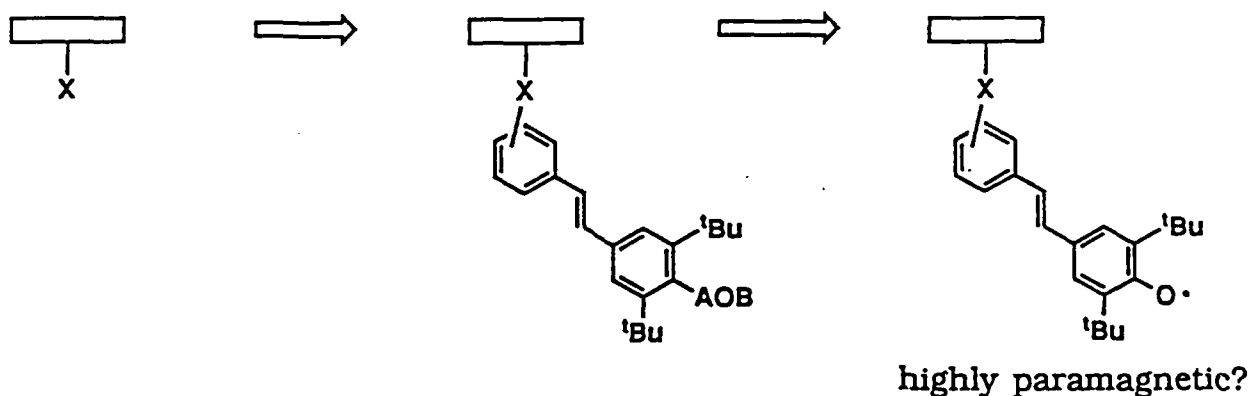
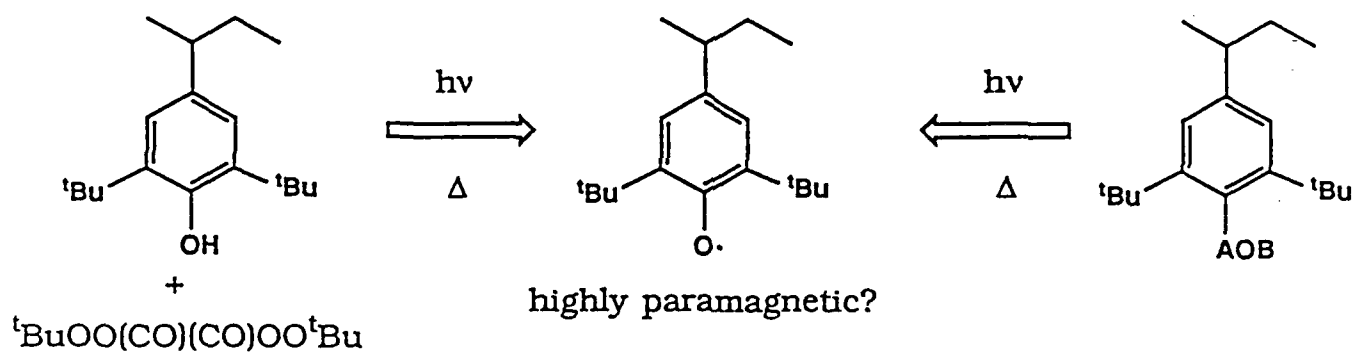
further functionalization
of this polymer to the
polyradical is desirable.

FUTURE WORK

1. Nitrenes and polynitrenes



2. Poly(2,6-di-*tert*-butyl-4-oxy-styrene) derivatives and copolymers. Polymers with pendant hindered stilbenoxy groups.



3. Optimize radical production in polymer matrices



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Group Members

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Frank Rossitto	Organic Magnetic Materials
Masaki Minato	Organic Magnetic Materials
Andrew Ichimura	Computational (Polyradicals)
Frank R. Denton III	Conducting Polymers
Ananda Sarker	Conducting Polymers
Mark Kearley	Pentamethylenepropanes

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